

obtained; m. p. 176°. *Anal.* Calcd. for $C_{14}H_{25}O_2N_2 \cdot HCl$: N, 9.77; Cl, 12.36. Found: N, 9.9; Cl, 12.4.



Fig. 2.—Amylcaine hydrochloride, hexagonal rod form, m. p. 176° ($\times 100$).

Between crossed nicols the crystals appeared as long rods with hexagonal cross section exhibiting negative elongation, sharp, parallel extinction and relatively low birefringence. In convergent polarized light partial uniaxial figures were observed, indicating particles with faces parallel to the optic axis. When the crystals were crushed, irregular angular fragments were obtained. An occasional particle did not extinguish sharply when the stage was revolved and in convergent polarized light exhibited a partial uniaxial figure. The optical character was negative. *Refractive indices:* $\omega = 1.582$; $\epsilon = 1.573$ (± 0.002).

Pseudomorphic Habit (Fig. 3).—When the lower melting form was kept at temperatures just below the melting point, the crystals became opaque and showed no tendency to melt at the lower temperature but melted sharply at 176°. This transformation could be followed readily by the change to a lower birefringence during the heating.

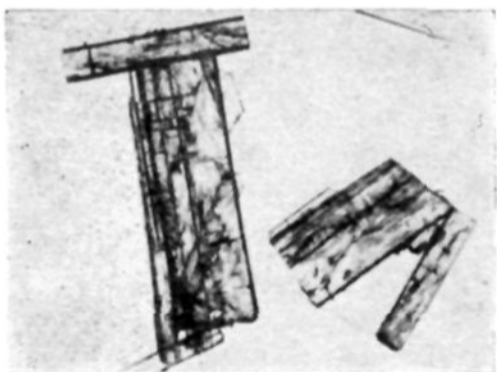


Fig. 3.—Amylcaine hydrochloride, pseudomorphic habit, m. p. 176° ($\times 100$).

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Sterols. CXLI. 3(α),11,12-Trihydroxycholanolic Acid¹

BY RUSSELL E. MARKER, ANTHONY C. SHABICA, ELDON M. JONES, HARRY M. CROOKS, JR., AND EMERSON L. WITTBECKER

We have repeated the work of Longwell and Wintersteiner² who attempted to prepare 3(α),11-

dihydroxycholanolic acid by the elimination of the keto group of 3(α),11-dihydroxy-12-ketocholanolic acid by the treatment with hydrazine hydrate and sodium ethylate at 200°. They obtained a compound having presumably two oxygen atoms less than the starting material.

We have obtained from this reaction a compound melting with decomposition at 136° with the empirical formula $C_{24}H_{40}O_5$ (II). The reduction of 3(α),11-dihydroxy-12-ketocholanolic acid (I) to 3(α),11,12-trihydroxycholanolic acid (II) is shown by the analysis and relative ease of its oxidation with chromic anhydride and subsequent Clemmensen reduction to neo-lithobilianic acid (III). Similarly neo-lithobilianic acid was obtained by the action of sodium ethylate and hydrazine hydrate on 11-hydroxy-12-ketocholanolic acid, followed by oxidation of the resulting dihydroxy compound. Reduction to the dihydroxy compound was the major product of both hydrazine reactions.

In addition we have oxidized directly 11-hydroxy-12-ketocholanolic acid to neo-lithobilianic acid. This product was not reported by Barnett and Reichstein³ who oxidized the methyl ester of 11-hydroxy-12-ketocholanolic acid under very mild conditions and obtained 11,12-diketocholanolic acid.

The reduction of a carbonyl to a carbinol group with hydrazine and alkoxide is not without analogy in the literature, for Marker and Lawson⁴ succeeded exclusively in converting pregnan-20(α)-ol-3-one to pregnanediol-3(α),20(α) by the Wolff-Kishner method. Later Dutcher and Wintersteiner⁵ in their investigation of this method of reduction of steroidal ketones showed in several cases that the conversion to a carbinol would take place in preference to the complete reduction to a methylene group.

We thank Parke, Davis and Company for their assistance.

Experimental Part

11,12-Dihydroxycholanolic Acid.—A mixture of 1 g. of 11-hydroxy-12-ketocholanolic acid, 5 cc. of 85% hydrazine hydrate, and 1.8 g. of sodium in 60 cc. of absolute ethanol was heated in a sealed tube for twelve hours at 200°. The product was diluted with water and extracted with ether. The aqueous layer was acidified and extracted with ether. The ether extract was washed with water, dried and evaporated. The product was crystallized from ether-

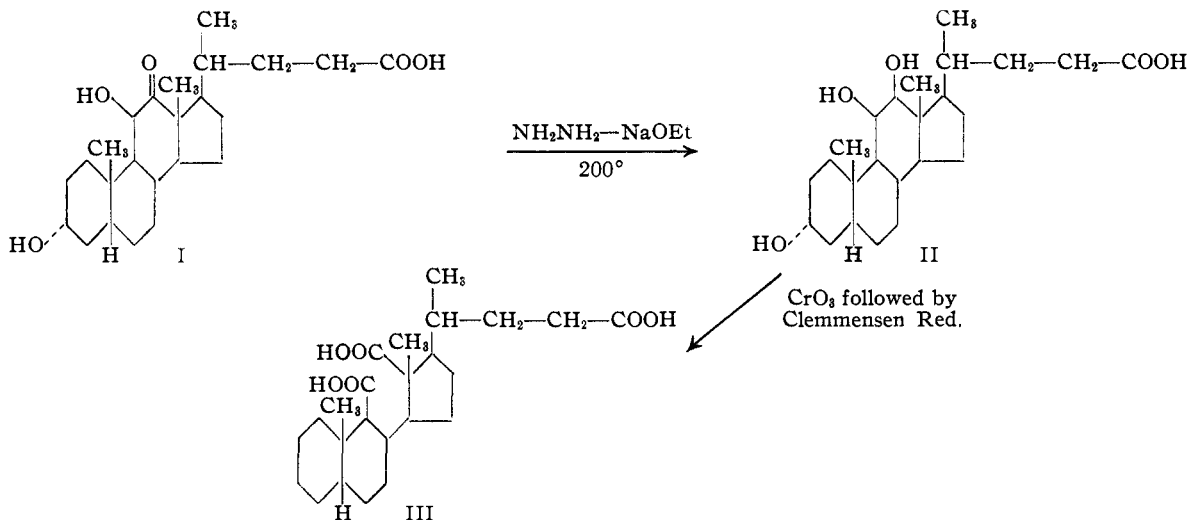
(3) Barnett and Reichstein, *Helv. Chim. Acta*, **XXI**, 926 (1938).

(4) Marker and Lawson, *THIS JOURNAL*, **61**, 852 (1939).

(5) Dutcher and Wintersteiner, *ibid.*, **61**, 1992 (1939).

(1) Original manuscript received June 27, 1941.

(2) Longwell and Wintersteiner, *THIS JOURNAL*, **62**, 200 (1940).



pentane and then from ethyl acetate; m. p. 204–208°; yield, 700 mg.

Anal. Calcd. for $\text{C}_{24}\text{H}_{40}\text{O}_4$: C, 73.4; H, 10.3. Found: C, 73.4; H, 10.4.

This compound was saturated as evidenced by the facts that it did not take up bromine and was recovered unchanged upon attempted hydrogenation with Adams catalyst in acetic acid.

neo-Lithobilianic Acid.—To a solution of 500 mg. of 11,12-dihydroxychoholic acid in 25 cc. of acetic acid was added a solution of 500 mg. of chromic anhydride in 15 cc. of 65% acetic acid. This mixture was allowed to stand at room temperature for one hour. The excess chromic anhydride was destroyed by adding zinc dust. The mixture was filtered and the filtrate was evaporated *in vacuo*. The residue was taken up in ether, washed with water, dried and the solvent was removed. The residue was crystallized from ether; m. p. 257–259°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C, 68.2; H, 9.1. Found: C, 68.4; H, 9.1.

In a similar manner 11-hydroxy-12-ketochoholic acid was oxidized to give a 25% yield of *neo-lithobilianic acid*; m. p. and mixed m. p. with the above acid, 257°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C, 68.2; H, 9.1. Found: C, 68.4; H, 9.2.

3(α),11,12-Trihydroxychoholic Acid.—A mixture of 2.5 g. of 3(α),11,12-dihydroxy-12-ketochoholic acid, 10 cc. of 85% hydrazine hydrate and a solution of 3.5 g. of sodium in 70 cc. of absolute ethanol was heated in a sealed tube for eight hours at 200°. The reaction mixture was worked up as described for 11,12-dihydroxychoholic acid. The product was crystallized from ether-pentane; m. p. 136° (bubbles); wt., 686 mg. It was also crystallized from ethyl acetate. This compound did not react with bromine and was recovered unchanged upon attempted catalytic reduction.

Anal. Calcd. for $\text{C}_{24}\text{H}_{40}\text{O}_5$: C, 70.5; H, 9.9. Found: C, 70.3; H, 9.8.

Oxidation of 3(α),11,12-Trihydroxychoholic Acid.—To a solution of 0.4 g. of 3(α),11,12-trihydroxychoholic acid in 40 cc. of acetic acid was added a solution of 0.4 g. of

chromic anhydride in 15 cc. of 65% acetic acid. This was allowed to stand at room temperature for one hour. Water was added to the mixture, and the precipitated solid was extracted with ether. The ether layer was washed with water and evaporated. A Clemmensen reduction was run on the residue by refluxing it with 50 cc. of ethanol, 10 g. of amalgamated zinc and adding 60 cc. of concentrated hydrochloric acid over a period of four hours. The zinc was filtered, and water was added to the filtrate. The product was extracted with ether and the ether layer was washed with water and evaporated. The residue was hydrolyzed with alcoholic potassium hydroxide. The free acid was crystallized from ether-pentane; m. p. and mixed m. p. with the *neo-lithobilianic acid* previously prepared, 256–259°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_6$: C, 68.2; H, 9.1. Found: C, 68.0; H, 9.0.

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Non-peroxide Catalysts for the Reaction between Sulfur Dioxide and Olefins¹

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A tertiary amine oxide, R_3NO , may be considered as a nitrogen analog of a peroxide and this has led us to try representatives of this group of compounds as catalysts for the addition of sulfur dioxide to an olefin or an acetylene to produce polymeric sulfones.

Trimethylamine oxide and dimethylaniline oxide proved to be catalysts for the reaction with such representative compounds as 1-pentene, 1-hexene, 1-heptene, 2-butene and 1-pentyne. The

(1) This is the thirteenth communication on the reaction between sulfur dioxide and olefins. For the twelfth see *THIS JOURNAL*, **61**, 2714 (1939).